

Chromium fluoride-containing bioactive glasses: Structure and properties

G-Eldamrawi, A K Hassan, M Abdelghany, H Al baghdady

Glass Research group, Physics Department, Faculty of Science, Mansoura University, 35516 Mansoura, Egypt.

ABSTRACT

Bioglasses in the system $24.5\text{Na}_2\text{O} \cdot 24.5\text{CaO} \cdot 6\text{P}_2\text{O}_5 \cdot x\text{CrF}_2 \cdot (45-x)\text{SiO}_2$ have been studied in the composition region of $x = 0-10$ mol%. CrF_2 Glass of molar ratio $(\text{Ca}+\text{Na})/\text{SiO}_2 \sim 1.1$ is the base material for the glasses containing different CrF_2 concentrations. X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Vicker hardness (H_v) measurements have been carried out. Crystalline feature of the glasses is followed up by XRD spectroscopy. It is found that crystallinity was enhanced via CrF_2 addition. More enhancement was confirmed via thermal heat treatment process. Increasing CrF_2 and sintering temperature will induce new ordered phases which will be distributed in the main glassy phase. Well formed fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) and wollastonite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ phases containing fluorine and chromium ions are evidenced in CrF_2 containing glasses. Increasing glass transition temperature T_g and hardness number H_v upon increasing CrF_2 concentration was discussed on bases of formation of additional bonds by the effect of CrF_2 molecules. The measured temperature window between T_c and T_g was found to have a great influence in material structure. Wide window is a feature of amorphous glass which free from CrF_2 . The window scale is found to quickly decrease with increasing CrF_2 , since crystalline phases are already formed in glasses containing CrF_2 . Formation of crystalline intermediate phases with more shielded silicate and phosphate structural is considered as the main reason for increasing T_g and (H_v) of the glasses. EDS as well as XRD analyzed spectra confirm that crystalline wollastonite of calcium inosilicate mineral (CaSiO_3) phase is well formed. The wollastonite species is evidenced to contain small amounts of chromium and fluorine ions which are substituting for calcium cations. Wollastonite phases with $\text{Cr}/\text{Si}=1$ is the most dominant type. This ratio is a characteristic feature of crystalline CaSiO_3 species. Small concentration from fluorine ions are involved in apatite phases. Presence of both crystalline apatite and wollastonite in the sample matrix promotes its biocompatibility, particularly orthopedic bioactivity. As a consequence, some of investigated glasses are recommended to be applicable in dental field of applications. This depends on its own crystallinity, hardness, its apatite and wollastonite concentration as biocompatible phases in the crystallized glass.

Keywords

Bioglasses, crystallization temperature, apatite biophases, chromium fluoride

Introduction

Some specific types of oxide glasses and glass ceramics can provide an appropriate biological response and result in the formation of a bond with the living tissues [1-5]. New modified dental materials are a derivative from bioactive glass ceramics which have different structures and properties when they compared with conventional glasses. Calcium phosphosilicate based material is well-known type which has bioactive and bio dental features are concerned in making bonds with natural tissues [4-7]. As a result, bioactive materials are known to have a wide range of medical and dental applications. They are currently used as a scaffold, bone graft, and coating materials for dental implants. Some of bioactive glasses are able to form HAP in few hours and can simply bind to tissues [6,7]

Safety of bioactive glasses was the main concern; therefore, different studies were performed to ensure that bioactive glasses are safe enough for clinical applications. Welson et al (1981) [8] have reviewed these studies and proposed that bioactive glasses are safe for clinical uses.

Most of previous studies [3-7] are based on SiO_2 containing glasses as stronger glass former. The importance of silicate glasses was appeared in stimulating gene activation and promote bone regeneration [9]. Phosphate is also considered to have an important consideration in view point of bioactivity. But in some cases, it was proved that P_2O_5 free glasses could also offer bioactivity [9,10]. Calcium ions play an important role in bone regeneration in terms of bone metabolism [8-10]. Some of calcium ions in Bioglass® are considered to be readily substituted with strontium or chromium ion which have been proven to uptake cellular activities and are effective for bone regeneration [10].

Recently, the bioactive glasses are modified to contain fluoride ions, since it prevents demineralization and enhances remineralization processes [10]. In addition, it has good activity in prevention secondary caries. The role of fluorine ion is appeared in forming fluorapatite phases which played the most effective influences on solubility of enamel [10]. Recent studies have been performed to shed more light on the role of F^- ions in properties and structure of bioactive glasses. It was reported that glasses containing CaF_2 is more biocompatible [5] and more safely to applied.

In the present work, the investigated glasses contain CaO and CrF_2 in the composition with an aim that CrF_2 can effectively enhance the structure and bioactivity of the investigated material. Understanding the structures of glasses and crystallized glasses is important for further applications such as plasma spray coating onto implant materials. In this work,



chromium fluoride -substituted bioactive glasses and their crystallized structure were analyzed using XRD, DSC, EDS and SEM techniques.

2. Experimental details

2.1. Sample preparation

Glass samples were prepared by using chemically pure SiO_2 , CaCO_3 , Na_2CO_3 , and CrF_2 . Using nominal composition 24.5Na₂O, 24.5CaO, 6 P₂O₅- xCrF₂ and (45-xSiO₂) mol% (where x =0, -10 mole %), The batches were accurately weighed out and then melted in alumina crucibles using an electric furnace at temperature 1200-1400°C. The melts were shocked well several times to achieve homogeneity. Each melt was stirred by rotating the crucible several times every 20 mins. The homogeneous melts were cast after an hour of melting into preheated stainless steel molds.

2.2 Measurement techniques

2.2.1. X-ray diffraction (XRD)

The amorphous or crystalline nature of the structure was observed by X-ray diffraction. XRD measurements were carried out on powdered samples at (Metallurgical Institute, El-Tebbeen- Helwan) using a Bruker D8 Advance powder XRD system with a ($\text{Cu K}\alpha$) radiation. The range of diffraction is changed from 10° to 70° using a dwell time of 0.4 seconds

2.2.2 Scanning electron microscope (SEM)

The morphology of the sample has been observed via (Scanning Electron Microscope unit, Mansura University) using a JEOL-JSM-6510 LV Model with a working accelerating voltage of 25 kV and an increasing size image up to 300.000X. The surface of the samples has been covered with a thin layer of gold before SEM measurement to withstand the environment inside the microscope.

2.2.3. Energy dispersive X-ray analysis (EDS)

The energy dispersive X-ray spectra (EDX) of the samples were also acquired during their scanning electron microscopic (SEM) measurement. The EDX spectrum normally involves peaks corresponding to X-rays generated by emission from different energy-levels in different elements. The higher concentrated elements in the sample present the most intense peaks in the spectrum. This technique is widely used for the identification of the elemental composition present in the sample.

2.2.4. Heat treatment (HT)

The selected samples containing 3 and 10 mol% CrF_2 , were heated in a muffle furnace (Heraeus KR170) controlled within $\pm 2^\circ\text{C}$. The samples were heat-treated at temperatures 500 °C and 600 °C for treatment time interval of 4 hours. After heating, the glasses were then kept into the furnace and held at the temperature of heat treatment for the desired time before cooling normally at room temperature.

2. 2.5 Differential Scanning Calorimetry

DSC analysis was carried out using a NETZSCH STA 409C/CD instrument. Known mass (≈ 30 mg) of crushed samples was placed into an aluminum pan then sealed with a crimped lid and heated from 25°C to 1000°C at a rate of 5°C/min with argon as carrier gas at a flow rate of 30 cm³ /min.

3 Results and Discussion

3.1 XRD Spectroscopy

Metal fluoride such (CrF_2) gives the glasses good advantages toward improvements of their biological properties like extremely high resistant to thermal shock, high mechanical strength, good chemical stability, crystallinity and bioactivity [11-13]. The advantage of the present glasses is that it can easily be crystallized by adding of even little concentration from CrF_2 to the host matrix. Extra structural and properties enhancement is considered through applying thermal heat treatment route as an effective controlling technique. In such situation, the glass can simply be transformed to glass ceramic with further controlled crystallization behavior.

It can be shown from figure 1 that, a small addition of CrF_2 to glasses has a profound effect on crystallization process which is achieved even at the reduced dopant level of CrF_2 (0.2 mol%). At lower concentration, for example (0 CrF_2) there is no any tendency toward crystallization. XRD pattern of chromium fluoride free glass (0 CrF_2) showed a broad hump which reflects the amorphous nature of the base glass. Amorphous orthophosphate (Na_3PO_4) and both calcium and sodium silicate mixed phases (CaSiO_3 and Na_2SiO_3) are the most dominant forming species [4,14] in base glass. On the other hand, few addition of CrF_2 (0.2 and 0.5 mol%) is found to have strong influence, since some XRD peaks superimposed on the wide diffracted hump are clearly appeared. The broad diffraction was eventually disappeared and more sharper peaks centered at about 22, 31, 34 and 47° were simply observed upon more CrF_2 addition. Different crystalline phases can be evidenced from the successfully increment in both sharpness and number of the diffraction peaks upon increasing CrF_2 contents. We suggest that, the base glass has already contained a high enough concentration of nuclei which are ready to aggregate to form crystalline phases by the help of dopant additive and /or sintering process.

Therefore, initial CrF_2 addition even with lower concentration (0.2 mol%) pushes the matrix toward crystallization. These changes lead one to suggest that CrF_2 can act as an enhancer for crystallization. This feature can be extracted from XRD patterns representing the studied glasses, since sharper peaks are evidenced upon increasing CrF_2 concentration, figure 1. These diffraction patterns are indexed to crystalline wollastonite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ [card no. 82-1914], and fourtopite crystalline $(\text{Ca}_5(\text{PO}_3)_3\text{F})$ [card no. 2-845]. In specific manner, both chromium silicate $(\text{Cr}_3(\text{Si}_3\text{O}_9))$ and the main crystalline phase from pseudowollastonite $(\text{Ca}_3(\text{Si}_3\text{O}_9))$ [4,14,15] are also evidenced to be constructed.

In terms of biocompatibility assessment, it could suggest that both the bioactivity and compatibility are attained, since both apatite and wollastonite crystals are documented to be present in the main glass matrix under the effect of CrF_2 addition. However, the highest extreme of crystallinity has not yet reached via CrF_2 addition. Alternatively, more enhanced phases can be obtained via sintering the glass at the onset of crystallization temperatures which is determined from DSC curves of the investigated glasses.

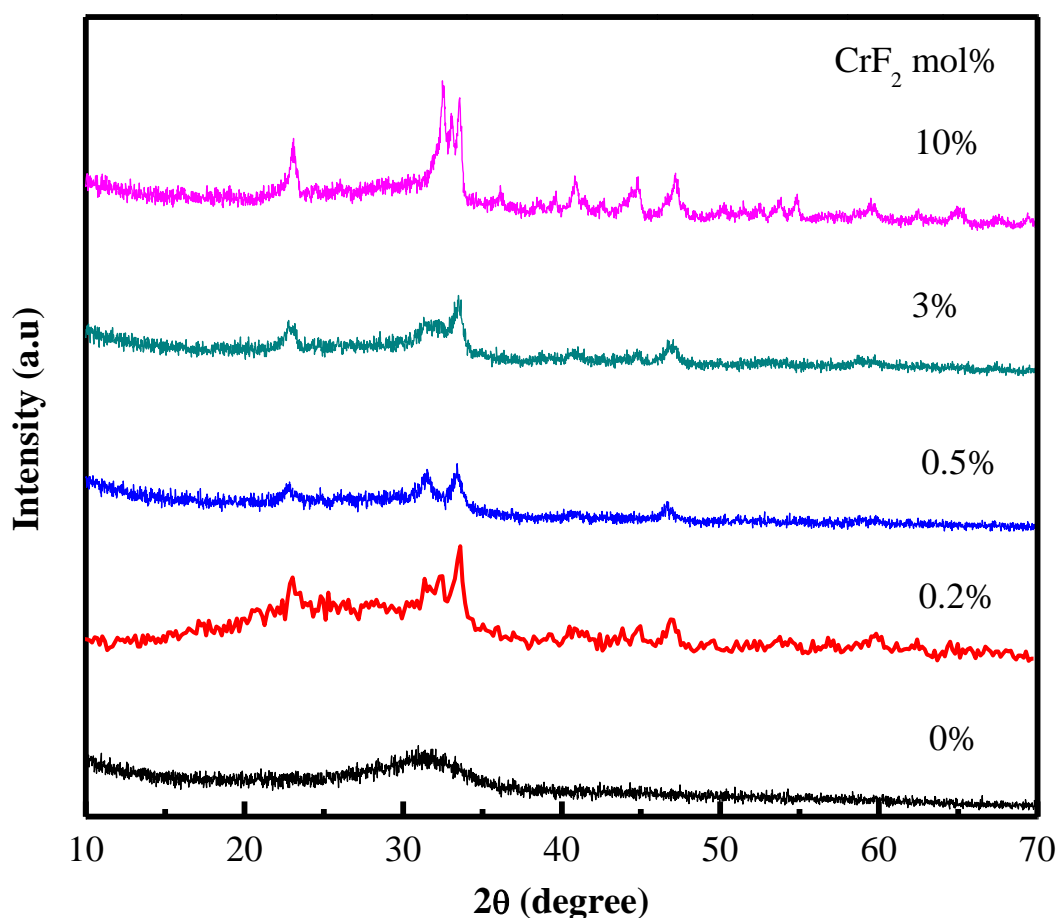


Figure 1 XRD patterns for glass containing 0, 0.2, 0.5, 3 and 10 mol% CrF_2

3.2 DSC and H_v results

DSC curves for glasses containing 0, 3 and 10 mol% CrF_2 are presented by figure 2(a-c). Both glass transition temperature (T_g) and peak crystallization temperature (T_c) are the two main features appeared in DSC curves. It can be realized that window between T_g and T_c is differed from one glass to another. This range is a guide for how the heat treating or sintering temperature can be rightly chosen to produce crystallized phases in glasses. For example, a wide processing range between the two parameters (T_g and T_c) gives an evidence that sinter process has little effect on crystallization. On the other hand, if the window between T_g and T_c is small, the material can undergo additional crystallization under effect of sintering temperature.

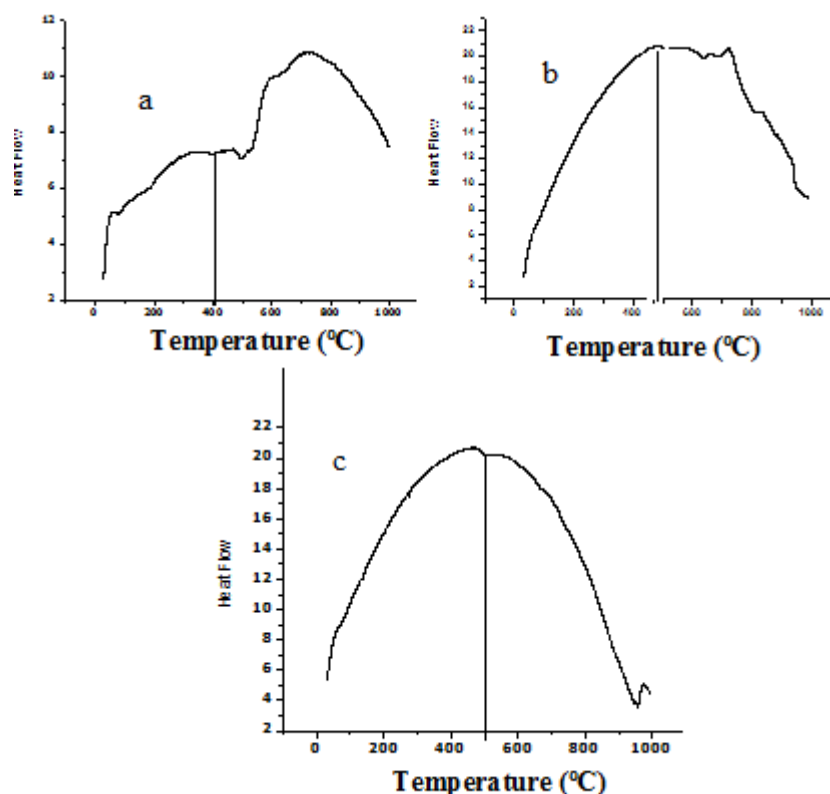


Figure 2 DSC curves for glasses containing 0 (curve a), 3 (curve b) and 10 (curve c) mol% CrF_2

The determined values of T_g was found to increase with increasing CrF_2 (figure 3). Increasing T_g with increasing CrF_2 concentration leads to increasing bond capacity. As a consequence the hardness number of the glass is shown also to increase with increasing CrF_2 concentration (see figure 4). Increasing both T_g and H_v with increasing CrF_2 is in harmony with decreasing window between T_c and T_g upon CrF_2 addition as is seen from figures 2(a-c). Relatively wider range between both T_g (400 °C) and onset of crystallization temperature (600 °C) for CrF_2 free glass is noticed. This wider range is referred to amorphous nature of the glass as confirmed from XRD pattern, figure 1. On the other hand, the window between T_c and T_g is continuously decreased with increasing CrF_2 concentration, figure 2(b-c), which reflect the crystalline nature of the glasses.

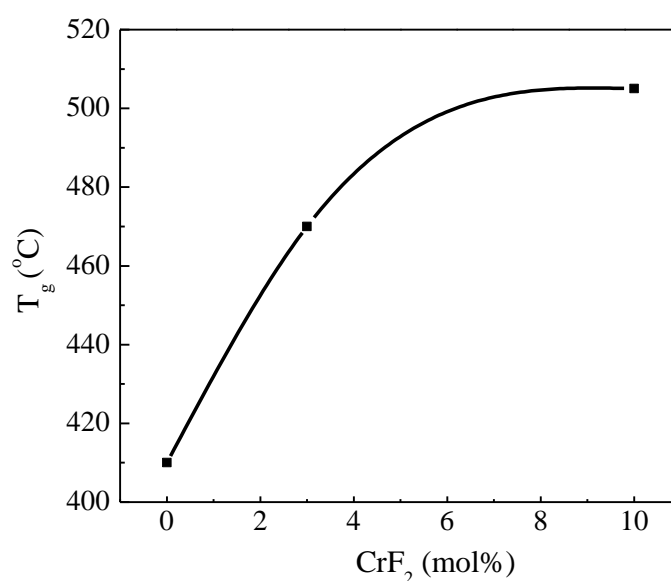


Figure 3 Change of T_g with CrF_2 concentration

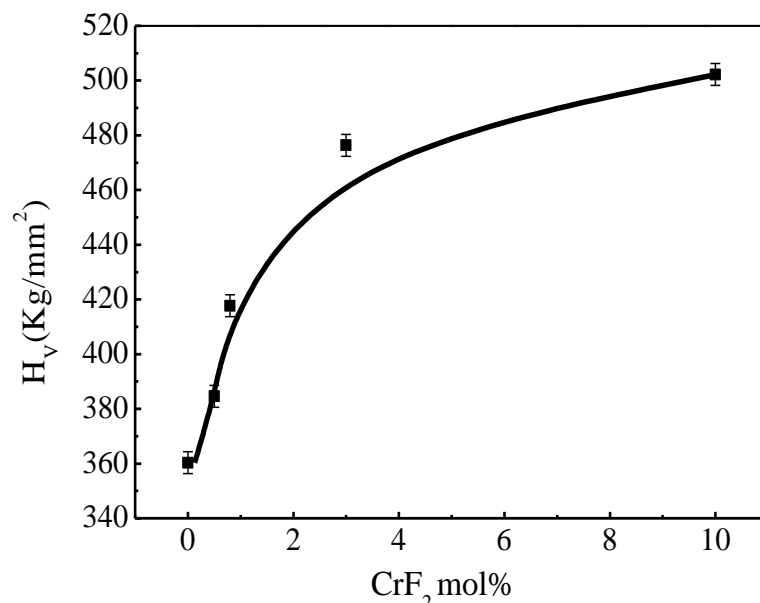


Figure 4 relationship between H_v and CrF_2 content

The above discussion leads one to consider that, sintering process will has more influences on glasses of high CrF_2 (10 mol%), since its T_c - T_g window is the smallest when it compared with that of glass containing 0 and 3 mol%. However, the selected glasses are all thermally sintered at the onset of glass transition T_g and also at the onset of crystallization temperature (600 °C). XRD measurements were carried out on some of the sintered glasses. The obtained results are compared with XRD patterns of as prepared glasses.

Figure 5 and 6 presented XRD of sintered glasses containing 3 and 10 mol% respectively. The glasses are thermally treated at 500 and 600 °C for 4 hours. It can be seen from these figures that the crystallinity is enhanced, particularly in glasses containing 10 mol% CrF_2 . New additional XRD peaks are appeared at 26, 29 and 51° which leads to inducing new additional crystalline phases under the effect of sintering process. The well resolved sharper XRD pattern at 34 and 47° are indexed to crystalline wollastonite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ [card no. 82-1914], and fluoroapatite crystalline $(\text{Ca}_5(\text{PO}_4)_3\text{F})$ [card no. 2-845]. For simplicity a comparison between XRD patterns for sintered glasses (at 600 °C) containing 3 and 10 mol% CrF_2 is presented in figure 7. A clear difference can be observed, since new peaks are only developed in glass of 10 mol% CrF_2 .

Glasses composed from the above given crystalline phases can play a main role in some of medical applications. They can be recommended to be used as useful inorganic counterpart of the glass ionomer cement (GIC) which is used as a dental restorative material [4,16-18]. The higher T_g , H_v and crystallinity of glass containing 10 mol% CrF_2 is highly recommended it for such biodental application.

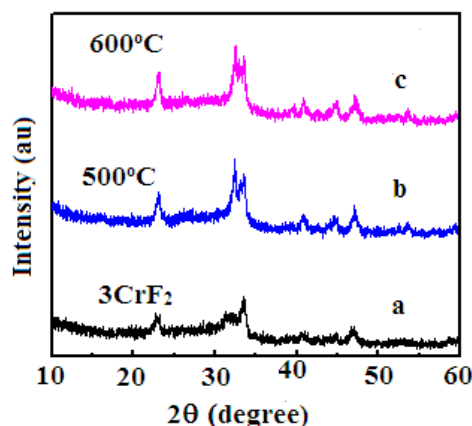


Figure 5 XRD patterns for glass containing 3 mol% CrF_2 (a), treated at 500 °C (b) and sintered at 600 °C (c) for 4 hrs.

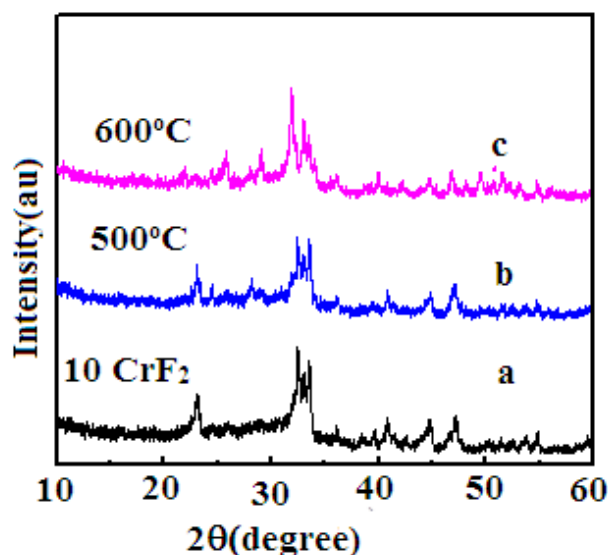


Figure 6 XRD patterns for glass containing 10 mol% CrF_2 (a), treated at 500 °C (b) and sintered at 600 °C (c) for 4 hrs.

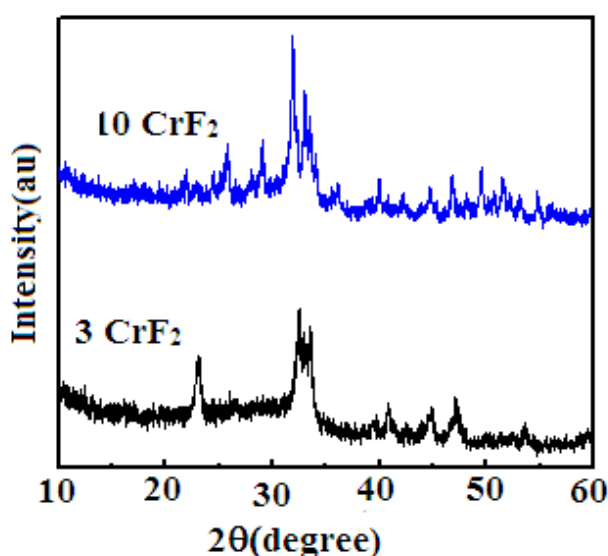


Figure 7 XRD patterns for glass containing 3 mol% and 10 mol% CrF_2 both treated at 600 °C for 4 hrs.

3.3 SEM and EDS spectroscopy

The morphological structure of the two glasses of 0 mol% CrF_2 and 10 mol% CrF_2 was analyzed using SEM micrographs under the same magnifications (see figure 8 (a,b)). As can be seen from the morphologies of particles, there is a limited distribution of small particles in sample of 0 mol% CrF_2 . On the other hand, large agglomerates are evidenced in micrograph of sample containing 10 mol%. These agglomerates consist of fine particles that could be welded together. The microstructure was observed to be almost like a needle and/or rod like shapes which characterize the crystalline wollastonite and apatite [1,4,15-20]. SEM images showed that the distributed nanoparticles were dense and highly concentrated evenly in glass which contain 10 mol% CrF_2 . In addition to this, although these smaller crystallites are so closely arranged together, a clear boundary between neighboring crystallites can still be observed, Fig. 8 (b)).

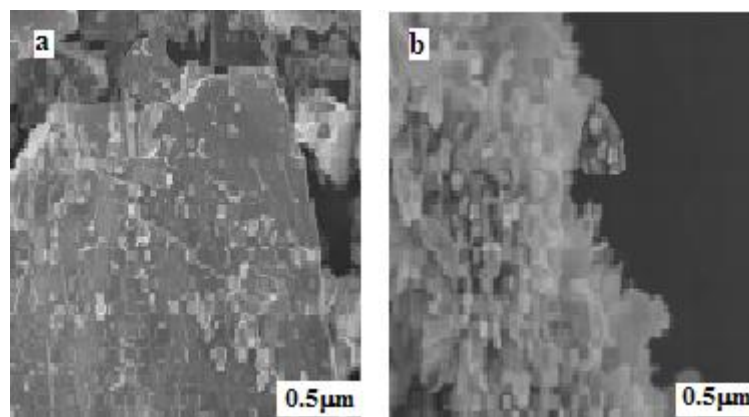


Figure 8 SEM of sample containing 0 mol% CrF_2 (a) and 10 mol% CrF_2 (b)

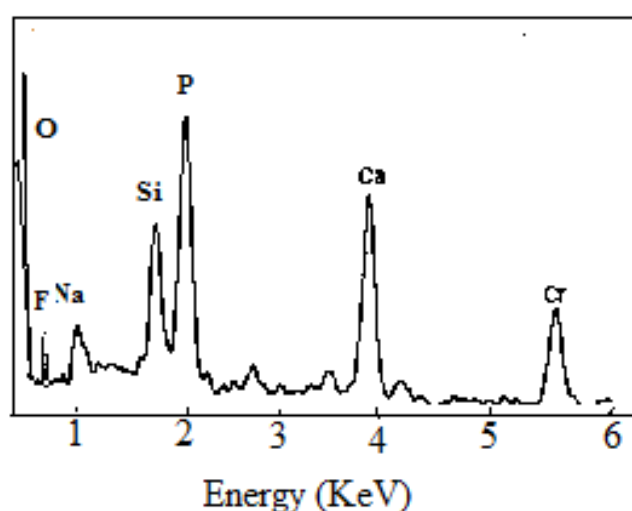


Figure 9 EDS spectra of glass containing 10 mol% CrF_2 .

The elemental composition has been investigated by the energy dispersion X-ray spectroscopy (EDS) analysis. Figure 9 shows EDS patterns of glass containing 10 mol% CrF_2 . From the EDS spectrum, the presence of Na, Ca, Si, Cr and O has been confirmed and the calculated percentages reveal almost the same ratio of $\text{CrO}_2/\text{SiO}_2$ CaO/SiO_2 as in crystalline wollastonite phases. EDS analysis ascertained that the crystallites of 10 mol% CrF_2 are composed of crystalline chromium silicate wollastonite phases, since the ratio of Cr/Si is found to be around unity which means that most of the phase constituent are found in its ordered state.

4 Conclusion

Bioglasses and glass ceramics containing different CrF_2 concentrations have been studied by different structural techniques. Amorphous nature of the glass free from CrF_2 is confirmed by XRD. Some types of crystalline species are formed in CrF_2 containing glasses. Well formed fluorapatite $(\text{Ca}_5(\text{PO}_4)_3\text{F})$ and wollastonite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$ phases containing fluorine and chromium ions are evidenced in CrF_2 containing glasses. More enhancement in crystallinity was confirmed via thermal heat treatment process. Wollastonite phases with $\text{Cr}/\text{Si}=1$ is the most dominant crystalline phase. Increasing glass transition temperature T_g and hardness number H_v upon increasing CrF_2 concentration was discussed on bases of formation of additional bonds by the effect of CrF_2 molecules. Presence of both crystalline apatite and wollastonite in the sample matrix promotes its biocompatibility, particularly orthopedic bioactivity.

References

- 1- -G. El-Damrawi , A. K. Hassan , H. Kamal*, M. Aboelez and S. Labeeb, British Journal of Applied Science & Technology, 16(3):(2016) 1-9
- 2- F. Baino. Journal of Biomedical Materials Research Part A. ;103(3)(2015):1259-1275.
- 3- . Z Hong, R L Reis, J F Mano. Materials Research Part A. 88(2) (2009);:304-313.
4. R Jayakumar, K Prasad Chennazhi, S Srinivasan, S V Nair, T Furuike, Hi Tamura. International Journal of Molecular Sciences. 12(3)(2011):1876- 1887.



- 5- G. El-Damrawi H. Doweidar H. Kamal A. Hassan, Silicon (2016)1-8
- 6--G El-Damrawi, H Kamal, H Doweidar, AE Dawood, British Journal of Applied Science & Technology 15(2)(2016)1
- 7- LL Hench, J Mat. Sci. Mater.Med 17(2006)967
- 8- J Willson,G.Piggot,F.Shoen, LL Hebch,J Biomed Mat Res.15(1981)805
- 9- Y.Ebisawa, T.Kokubo, K.Yamamuro, J.Mater.Sci. Chromium, vanadMat/Med.1(1990)230.
- 10- M Wei,JH Evans T Bostrom L Grondahl J Mat. Sci. Mater.Med 14(2003) 3 11.
- 11- H Doweidar, G El-Damrawi, M Abdelghany, Physics and Chemistry of Glasses-European Journal of Glass Science and Technology Part B,55(4)(2014) 167-175
- 12- E. Auffray, D. Bouttet, I. Dafinei, J. Fay, P. Lecoq, J.A. Mares, M. Martini, G. Mazé, F. Meinardi, B. Moine, M. Nikl, C. Pedrini, M.Poulain, M. Schneegans, S. Tavernier, A. Vedda, European organization for nuclearresearch CERN-PPE / 96-35 CERN, February 9th, 1996
- 13- M.Nikl, J.A.Mares, E.Mihokova, A.Beitlerova, K.Blazek, J.Jindra: Sol. St. Comm. 87, (1993) 185.
- 14- H.ESLAMI, M. SOLATI-HASHJIN, M. TAHRIRI , F. BAKHSHI Materials Science-Poland, 28(2010)1
- 15- G DO` Rsami , A Liebscher, B Wunder, G Franz and M GottschalkEur. J. Mineral. 21 (2009) 705–714
- 16- LL Hench , Bioactive – from concept to clink, J.Am.Soc.74(1991)1487
- 17- JR Jones,EGentelman, J Polak, Elements 3(2007)393
- 18-MR Toler,CMCrowley, D Murphy, J Material Science Letter 21(2002)1123
- 19- H Ali, J Den 3 (2012)199
- G. El-Damraw H. Doweidar H. Kamal, Silicon (2014)1-7